Multi-Photon Absorption

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Two-Photon Absorption

A general two-photon absorption experiment involves two laser beams of different frequencies, polarizations and directions. For this theoretical development, this translates to consideration of two modes of the radiation field, $(\vec{k_1}, \hat{\epsilon}_1)$ and $(\vec{k_2}, \hat{\epsilon}_2)$. Using some detection scheme, be it subsequent fluorescence or photo-ionization, acoustic, thermal lensing or birefringence, the probability of creating the final state $|b\rangle$ is measured.

To calculate the probability of finding the system changing from $|a\xi_a\rangle$ to $|b\xi_b\rangle$ during the time interval t we need to take the absolute square of

$$U_{ba} = \left(-\frac{i}{\hbar}\right)^2 e^{-\frac{i}{\hbar}E_b t} \int_0^t \int_0^{t_1} \langle b\xi_b| e^{\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t_1} \left[-\frac{2e}{m}\vec{A}(\vec{r},t_1)\cdot\vec{p}\right] e^{-\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t_1} e^{\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t_2} \left[-\frac{2e}{m}\vec{A}(\vec{r},t_2)\cdot\vec{p}\right] e^{-\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t_2} |a\xi_a\rangle\, dt_1\, dt_2\,. \quad (1)$$

To evaluate

$$U_{ba} = \left(-\frac{i}{\hbar}\right)^2 e^{-\frac{i}{\hbar}E_b t} \int_0^t \int_0^{t_1} e^{\frac{i}{\hbar}E_b t_1} \langle b\xi_b| \left[-\frac{2e}{m}\vec{A}(\vec{r},t_1)\cdot\vec{p}\right] e^{-\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t_1} e^{\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t_2} \left[-\frac{2e}{m}\vec{A}(\vec{r},t_2)\cdot\vec{p}\right] |a\xi_a\rangle e^{-\frac{i}{\hbar}E_a t_2}\, dt_1\, dt_2\,, \quad (2)$$

we will insert a complete set of states between the two operators

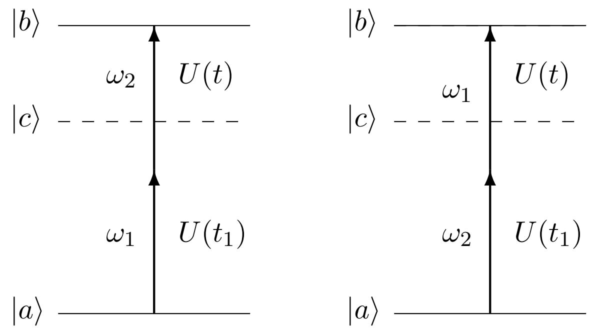
$$\sum_j \langle b\xi_b| \left[-\frac{2e}{m}\vec{A}(\vec{r},t_1)\cdot\vec{p}\right] e^{-\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t_1} |c\xi_c\rangle\langle c\xi_c| e^{\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t_2} \left[-\frac{2e}{m}\vec{A}(\vec{r},t_2)\cdot\vec{p}\right] |a\xi_a\rangle\,. \quad (3)$$

This is exact only if the set of states $[|c\rangle]$ is truly complete, and this insertion is not necessary but useful. Focusing on just the t_2 integral,

$$-\frac{2e}{m}\int_0^{t_1} e^{\frac{i}{\hbar}E_c t_2} \langle c\xi_c| \left[A_1\, a_1 \hat{\epsilon_1}\, e^{i(\tilde{k}_1\cdot\tilde{r}-\omega_1 t_2)} + A_2\, a_2 \hat{\epsilon_2}\, e^{i(\tilde{k}_2\cdot\tilde{r}-\omega_2 t_2)}\right]\cdot\vec{p}|a\xi_a\rangle e^{-\frac{i}{\hbar}E_a t_2}\, dt_2$$
$$= -\frac{2e}{m}\int_0^{t_1} e^{\frac{i}{\hbar}E_c t_2} \langle c\xi_c| A_1\, a_1 \hat{\epsilon_1}\, e^{i(\tilde{k}_1\cdot\tilde{r}-\omega_1 t_2)}\cdot\tilde{p}|a\xi_a\rangle e^{-\frac{i}{\hbar}E_a t_2}\, dt_2 - \frac{2e}{m}\int_0^{t_1} e^{\frac{i}{\hbar}E_c t_2} \langle c\xi_c| A_2\, a_2 \hat{\epsilon_2}\, e^{i(\tilde{k}_2\cdot\tilde{r}-\omega_2 t_2)}\cdot\tilde{p}|a\xi_a\rangle e^{-\frac{i}{\hbar}E_a t_2}\, dt_2\,. \quad (4)$$

Thus, we have two different time-orderings: ω_1 followed by ω_2 and vice versa. There are also terms in eq. 1 which describe absorption of two ω_1 photons and two ω_2 photons, but these will be ignored. Thus, eq. 1 will be described diagrammatically by the pictures below.

(1) (2)



At this point is it necessary to convert the operator

$$a_j \hat{\epsilon}_j e^{i(\vec{k}_j \cdot \vec{r} - \omega_j t_j)} \cdot \vec{p} \tag{5}$$

into a more convenient operator. The first approximation is refered to as the electric dipole approximation. Notice that when the wavelength is large compared to the dimensions of the quantum system (molecule), then the exponential operator is approximately constant for all values of $\vec{r}$ in the integral:

$$\begin{aligned} e^{i(\vec{k}_j \cdot \vec{r} - \omega_j t)} &= e^{i(\vec{k}_j \cdot (\vec{r}_\circ + \vec{r}') - \omega_j t)} = e^{i(\vec{k}_j \cdot \vec{r}_\circ - \omega_j t)} e^{i\vec{k}_j \cdot \vec{r}'} \\ &= e^{i(\vec{k}_j \cdot \vec{r}_\circ - \omega_j t)} [1 + i\vec{k}_j \cdot \vec{r}' + \cdots] \approx e^{i(\vec{k}_j \cdot \vec{r}_\circ - \omega_j t)} . \end{aligned} \tag{6}$$

The origin of the molecule is define as $\vec{r}_\circ$. The phase factor $e^{i\vec{k}_j \cdot \vec{r}_\circ}$ is of no significance for incoherent phenomena, since taking an absolute square will eliminate it, but will be important in coherent nonlinear optical phenomena where the amplitude is the important quantity. Now, the operator is simple $\hat{\epsilon}_1 \cdot \vec{p}$, and the previous transformation from the momentum to the length form of an integral can be invoked.

$$\begin{aligned} \langle c\xi_c | a_j \hat{\epsilon}_j \cdot \vec{p} | a\xi_a \rangle &= \frac{m}{i\hbar}(E_a - E_c) \langle c\xi_c | a_j \hat{\epsilon}_j \cdot \vec{r} | a\xi_a \rangle \\ &= im(\omega_c - \omega_a) \langle c\xi_c | a_j \hat{\epsilon}_j \cdot \vec{r} | a\xi_a \rangle = im\omega_{ca} \langle c\xi_c | a_j \hat{\epsilon}_j \cdot \vec{r} | a\xi_a \rangle . \end{aligned} \tag{7}$$

Thus,

$$\langle b\xi_b | a_j \hat{\epsilon}_j e^{i(\vec{k}_j \cdot \vec{r} - \omega_j t)} \cdot \vec{p} | a\xi_a \rangle = e^{i(\vec{k}_j \cdot \vec{r}_\circ - \omega_j t)} im\omega_{ca} \langle c\xi_c | a_j \hat{\epsilon}_j \cdot \vec{r} | a\xi_a \rangle , \tag{8}$$

will be used in the expression for U_{ba}. The annihilation operator a_j only operates on the number state $|n_j\rangle$ of the field. This results in the expression

$$\begin{aligned} \langle c\xi_c | a_j \hat{\epsilon}_j \cdot \vec{r} | a\xi_a \rangle &= \langle c | \hat{\epsilon}_j \cdot \vec{r} | a \rangle \langle \xi_b | a_j | \xi_a \rangle = \langle c | \hat{\epsilon}_j \cdot \vec{r} | a \rangle \sqrt{n_{ja}} \langle n_{jb} | n_{ja} - 1 \rangle \\ &= \langle c | \hat{\epsilon}_j \cdot \vec{r} | a \rangle \sqrt{n_{ja}} \delta_{n_{jb} n_{ja} - 1} = \langle c | r_j | a \rangle \sqrt{n_{ja}} \delta_{n_{jb} n_{ja} - 1} , \end{aligned} \tag{9}$$

which should simplify the notation considerably.

Evaluation of an integral over t_2 yields

$$-\frac{2e}{m}A_j\, e^{i(\tilde{k}_j\cdot\tilde{r}_\circ)} im\omega_{ca}\langle c|r_j|a\rangle\sqrt{n_{ja}}\delta_{n_{jc}n_{ja}-1}\int_0^{t_1} e^{(\frac{i}{\hbar}(E_c-E_a)-\omega_j)t_2}\,dt_2$$
$$=-\frac{2e}{m}A_j\, e^{i(\tilde{k}_j\cdot\tilde{r}_\circ)} im\omega_{ca}\langle c|r_j|a\rangle\sqrt{n_{ja}}\delta_{n_{jc}n_{ja}-1}\frac{-i}{(\omega_{ca}-\omega_j)}\left[e^{i(\omega_{ca}-\omega_j)t_1}-1\right]\,, \quad (10)$$

where $j=\omega_1$ or ω_2. Ignoring the -1 in the brackets as an artifact of choosing $t=0$ as the time at which the field appeared, the second integration over t_1 for the case of ω_1 followed by ω_2 is simple because of the requirement for energy conservation

$$\omega_{bc}+\omega_{ca}-\omega_1-\omega_2=\omega_b-\omega_c+\omega_c-\omega_a-\omega_1-\omega_2=0\,. \quad (11)$$

So,

$$\left(\frac{2e}{m}\right)^2 A_2\, e^{i(\tilde{k}_2\cdot\tilde{r}_\circ)} im\omega_{bc}\langle b|r_2|c\rangle\sqrt{n_{2c}}\delta_{n_{2b}n_{2c}-1}A_1\, e^{i(\tilde{k}_1\cdot\tilde{r}_\circ)} im\omega_{ca}\langle c|r_1|a\rangle\sqrt{n_{1a}}\delta_{n_{1c}n_{1a}-1}$$
$$\frac{-i}{(\omega_{ca}-\omega_1)}\int_0^t e^{(\frac{i}{\hbar}(E_b-E_c)-\omega_2)t_1}e^{i(\omega_{ca}-\omega_1)t_1}\,dt_1$$
$$=4e^2A_2\, e^{i(\tilde{k}_2\cdot\tilde{r}_\circ)} i\omega_{bc}\langle b|r_2|c\rangle\sqrt{n_{2c}}\delta_{n_{2b}n_{2c}-1}A_1\, e^{i(\tilde{k}_1\cdot\tilde{r}_\circ)} i\omega_{ca}\langle c|r_1|a\rangle\sqrt{n_{1a}}\delta_{n_{1c}n_{1a}-1}\frac{-i}{(\omega_{ca}-\omega_1)}t$$
$$=i4e^2A_1A_2\, e^{i(\tilde{k}_1+\tilde{k}_2)\cdot\tilde{r}_\circ}\omega_{bc}\omega_{ca}\sqrt{n_{2c}}\sqrt{n_{1a}}\delta_{n_{2b}n_{2c}-1}\delta_{n_{1c}n_{1a}-1}\frac{\langle b|r_2|c\rangle\langle c|r_1|a\rangle}{(\omega_{ca}-\omega_1)}t\,. \quad (12)$$

Adding both time-orderings and simplifying the notation a bit yields

$$U_{ba}=i4e^2A_1A_2\, e^{i(\tilde{k}_1+\tilde{k}_2)\cdot\tilde{r}_\circ}\sqrt{n_2}\sqrt{n_1}\,t\sum_c\omega_{bc}\omega_{ca}\left[\frac{\langle b|r_2|c\rangle\langle c|r_1|a\rangle}{(\omega_{ca}-\omega_1)}+\frac{\langle b|r_1|c\rangle\langle c|r_2|a\rangle}{(\omega_{ca}-\omega_2)}\right]\,, \quad (13)$$

and the probability of the transition $a\to b$ is $|U_{ba}|^2$. Note that $|U_{ba}|^2$ is proportional to the product of field intensities I_1I_2. Phenomenological damping corrections $\omega_{ca}\to\omega_{ca}-i\Gamma_c$ are required to keep U_{ba} finite when a resonance condition $\Re(\omega_{ca})=\omega_j$

To discuss selection rules for a two-photon transition, that is list of allowed and forbidden transitions for given polarizations and propagation directions, the symmetry of the the matter states will be considered in construction of the matrix

$$\mathbf{S}=\sum_c\left[\frac{\langle b|r_j|c\rangle\langle c|r_i|a\rangle}{(\omega_{ca}-\omega_1)}+\frac{\langle b|r_i|c\rangle\langle c|r_j|a\rangle}{(\omega_{ca}-\omega_2)}\right]\,, \quad (14)$$

for which $r_{i,j}=x,\ y,$ or z $\mathbf{S}$ is used to determine U_{ba} through

$$U_{ba}=\mathbf{S}\hat{\epsilon}_1\hat{\epsilon}_2=\sum_{i,j=x,y,z}S_{ij}\epsilon_{1i}\epsilon_{2j}\,. \quad (15)$$

. The integrals will be zero if the integrand is antisymmetric with respect to some symmetry operation of the molecule, or, speaking in group theoretic terms, does not transform as the basis of the totally symmetric repesentation of the group of symmetry operations of the molecule.